Reversible Polymerization and Cis−Trans Isomerization Equilibria in $[PdCl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]$ Metallacrown Ethers

Dale C. Smith, Jr., and Gary M. Gray*

Department of Chemistry, CHEM201 UAB Station, The University of Alabama at Birmingham, Birmingham, Alabama 35294-1240

Received October 1, 1997

The first study of metallacrown ethers with kinetically labile metal centers is reported. The reaction of $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ with $PdCl_2$ in an acetonitrile−dichloromethane solution yields an equilibrium mixture of cyclic *n*-mers and monomers with the empirical formula $[PdCl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]$. Both cis and trans coordination geometries are observed for the palladium(II) in these complexes, with the trans being the more abundant. The solution equilibria in both chloroform-*d* and acetonitrile-d_3 were studied using $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopy. A model has been developed relating the product distributions at various concentrations, obtained from integration of quantitative $^{31}P\{^1H\}$ NMR spectra, to a cis−trans equilibrium constant and equilibrium constants for the dimerization and *n*-merization reactions of the trans monomer. The concentration and temperature dependence of the equilibrium constants obtained from this model are consistent with the thermodynamics of cis−trans isomerization and reversible step polymerization. One surprising result from this study is that the dimerization equilibrium constant is nearly an order of magnitude smaller than the *n*-merization equilibrium constant.

Introduction

Chelation of α,ω-bis(phosphorus donor)-polyether ligands to transition metals yields a class of complexes called metallacrown ethers.[1] We have shown that these complexes are similar to the crown ethers[2] and related *metalloreceptors*[3] in that they are capable of binding alkali metal cations and small molecules.[1,4] Analogous to crown ethers,[2] metallacrown ethers have cation-binding selectivities that depend on the relative sizes of the cation and the metallacrown ether ring.[1,4]

Metallacrown ethers containing platinum-group metals could exhibit interesting catalytic activities and selectivities for organic reactions[5] involving ionic[6,7] or bifunctional substrates[8,9] because of their ability to form guest−host complexes. However, our initial investigations of the $[PdCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]$ (n = 3, 5) metallacrown ethers indicated that a number of chromatographically inseparable complexes with this empirical formula are present in solution.[10] Similar solution behavior has been reported for $PdX_2\{R_2P(CH_2)_nPR_2\text{-}P,P'\}$ (X = Cl, Br, I; n = 8−12) complexes and is poorly understood.[11−15]

We have begun a study to identify the species present in solutions of the $[PdCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]$ (n = 3−5) metallacrown ethers. This paper reports the results from a detailed $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopic study of the n = 4 complex and of $[PdCl_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_3\text{-}P\}]$, a model complex with monodentate phosphine ligands. This study demonstrates that the numerous species in the solutions of the n = 4 complex are at equilibrium and presents a mathematical model for describing their solution equilibria.

Experimental Section

General Procedures. All starting materials, free ligands, and deuterated solvents were handled under a dry nitrogen atmosphere using

(1) (a) Gray, G. M. *Comments Inorg. Chem.* **1995**, *17*, 95−114. (b) Gray, G. M.; Duffey, C. H. *Organometallics* **1995**, *14*, 238−244. (c) Gray, G. M.; Duffey, C. H. *Organometallics.* **1995**, *14*, 245−250. (d) Varshney, A.; Gray, G. *Inorg. Chem.* **1991**, *30*, 1748−1754.
(2) Vogtle, F. *Host Guest Complexes Chemistry II*; Springer-Verlag: Berlin, Heidelberg, New York, 1982; 1−81.
(3) (a) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, U.K., 1989. (b) van Veggel, F. V. J. M.; Verboom, W.; Reinhoudt, D. N. *Chem. Rev.* **1994**, *94*, 279−299. (c) Cameron, B. R.; Corrent, S. S.; Loeb, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 23−24.
(4) Gray, G. M.; Fish, F. P.; Duffey, C. H. *Inorg. Chim. Acta* **1996**, *246*, 229−240.
(5) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Rauchfuss, T. B. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York and London, 1983.
(6) (a) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis Principles and Techniques*; Academic Press: New York, 1978; Chapter 2. (b) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 3rd ed.; VCH Verlagsgesell mbH: Weinheim, Germany; VCH Publishers: New York, 1993. (c) Starks, C. M.; Alper, H. *Phase-Transfer Catalysis New Chemistry, Catalysts, and Applications* ACS Symposium Series 326; American Chemical Society; Washington, D.C., 1987. (d) Okano, T.; Iwahara, M.; Kiji, J. *Chem. Lett.* **1986**, 1467−1470. (e) Okano, T.; Yamamoto, M.; Noguchi, T.; Konishi, H.; Kiji, J. *Chem. Lett.* **1982**, 977−980.
(7) (a) Cotesee, N. A.; Heck, R. F. *J. Org. Chem.* **1977**, *42*, 3491−3494. (b) Pri-Bar, I.; Buchman, O. *J. Org. Chem.* **1986**, *51*, 734−741. (c) Spatola. A. F. *J. Org. Chem.* **1989**, *54*, 1284−1287. (d) Grushin, V. V.; Bensiomon, C.; Alper, H. *Organometallics* **1995**, *14*, 3259−3263.
(8) (a) McLain, S. J. *J. Am. Chem. Soc*. **1983**, *105*, 6355−6357. (b) McLain, S. J.; Waller, F. J. U.S. Patent 4,432,904, 1984. (c) McLain, S. J. *Chem. Abstr*. **1984**, 100, 210 158a.
(9) (a) Okano, T.; Hayashi, T.; Kiji, J. *Bull. Chem. Soc. Jpn*. **1994**, *67*, 2329−2332. (b) Okano, T.; Harada, N.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2339−2341. (c) Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 452−461. (d) Tanaka, M.; Kobayashi, T.; Sakakura, T. *J. Chem. Soc., Chem. Commun.* **1985**, 837−838. (e) Grushin, V. V.; Alper, H. *J. Am. Chem. Soc*. **1995**, *117*, 4305−4315. (f) Pri-Bar, I.; Buchman, O. *J. Org. Chem*. **1988**, *53*, 624-626. (g) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1816−1817. (h) Yamamoto, A. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 433−446.

S0020-1669(97)01249-4 CCC: $15.00
Published on Web 03/20/1998

standard Schlenk techniques. The palladium complexes are air stable and required no special handling precautions. Pentaethylene glycol, methanesulfonyl chloride, and di(ethylene glycol) ethyl ether were distilled before use. Triethylamine was purified by distillation from potassium hydroxide and then from calcium hydride. Tetrahydrofuran was distilled from sodium-benzophenone, and both dichloromethane and acetonitrile were distilled from calcium hydride before use. Elemental analyses were performed by Atlantic Microlabs of Norcross, GA.

Multinuclear ($^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H) NMR spectra were recorded on a Bruker ARX300 FT-NMR spectrometer with a variable temperature accessory. The ^1H NMR chemical shifts were referenced to internal tetramethylsiliane (TMS), and the $^{13}C\{^1H\}$ shifts were referenced either to chloroform-*d* (77.0 ppm) or internal TMS. The $^{31}P\{^1H\}$ chemical shifts were referenced to external 85% phosphoric acid (capillary) in chloroform-*d*. All downfield chemical shifts are reported as positive. Sample temperatures (±1 K) were recorded with an external thermocouple and were calibrated with ethylene glycol using standard procedures.[16]

Synthesis of $CH_3SO_2(OCH_2CH_2)_2OCH_2CH_3$ (1). A solution of 2.50 mL (32.0 mmol) of methane sulfonyl chloride in 25 mL of dichloromethane was added to a stirred solution of 3.83 g (28.5 mmol) of di(ethylene glycol) ethyl ether and 4.5 mL (32.0 mmol) of triethylamine in 75 mL of dichloromethane at ambient temperature over a 2-h period. The mixture was evaporated to dryness, and the oily residue was treated with 200 mL of benzene. The resulting mixture was filtered through a medium frit containing Celite to give a clear, colorless filtrate. The filtrate was evaporated to dryness in vacuo (0.02 mmHg at 295 K for 48 h) to yield 5.13 g (84.8%) of **1** as a hygroscopic, colorless oil. This oil was characterized by its ^1H NMR spectra and was subsequently used in the successful synthesis of **2**. ^1H NMR (chloroform-*d*, 300 MHz, δ): 3.06 (s, 3H, CH_3SO_2); 4.48 (m, 2H, SO_2OCH_2); 3.42−3.82 (m, 8H, OCH_2); 1.22 (m, 3H, CH_2CH_3).

Synthesis of $Ph_2P(CH_2CH_2O)_2CH_2CH_3$ (2). A solution of 3.93 g (24.1 mmol) of **1** in 75 mL of tetrahydrofuran was stirred at ambient temperature as 21 mL of a 0.5 M solution of potassium diphenylphosphide in tetrahydrofuran was added dropwise over 30 min. The reaction of mixture was stirred for 18 h and then evaporated to dryness in vacuo (21 mmHg at 315 K for 2 h) to yield an oily residue. The residue was treated with 50 mL of dichloromethane, and the mixture was extracted with deionized water (3 × 100 mL) to remove the potassium methanesulfonate byproduct. The dichloromethane layer was dried over magnesium sulfate and then filtered through Celite. The filtrate was evaporated to dryness in vacuo (0.02 mmHg at 295 K for 24 h) to yield a yellow oil. Fractional distillation of the crude oil yielded 4.12 g (57.0%) of **2** as a colorless oil distilling between 401 and 410 K at 0.050 mmHg. The free ligand **2** was characterized by its ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra and was subsequently used in the successful synthesis of **3**. ^1H NMR (chloroform-*d*, 300 MHz, δ): 1.1 (m, 3H, CH_3); 2.3 (m, 2H, PCH_2); 3.2−3.6 (m, 8H, OCH_2); 7.1−7.6 (m, 10H, C_6H_5P).

Synthesis of $[PdCl_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_3$-*P*$\}_2]$ (3). A solution of 0.266 g (1.50 mmol) of palladium(II) dichloride and 0.910 g (3.00 mmol) of **2** in 50 mL of a 2:1 acetonitrile−dichloromethane mixture was stirred at ambient temperature for 24 h and then filtered. Evaporation of the filtrate to dryness in vacuo (0.02 mmHg at 295 K) produced a hard orange-yellow oil. Recrystallization of this oil from a dichloromethane−hexanes mixture yielded 1.03 g (87.2%) of analytically pure **3** as orange-yellow crystals. ^1H NMR (chloroform-*d*, 300 MHz, δ): 1.1 (m, 6H, CH_3); 2.6−2.9 (m, 4H, PCH_2); 3.4−3.8 (m, 16H, OCH_2); 7.1−7.7 (m, 20H, C_6H_5P). Anal. Calcd for $C_{36}H_{46}Cl_2O_4P_2Pd$: C, 55.29; H, 5.93; Cl, 9.07. Found: C, 55.03; H, 5.96; Cl, 9.14.

Synthesis of $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ (4). The free ligand, **4**, was prepared by a modification of the previously published method[17] in which a commercially available solution of potassium diphenylphosphide in tetrahydrofuran was substituted for a solution of lithium diphenylphosphide, which was prepared from the reaction of diphenylphosphine with a solution of *n*-butyllithium in hexanes. These two methods give comparable yields of **4**.

Synthesis of $[PdCl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′$\}]$ (5). A mixture of 1.04 g of palladium(II) dichloride (5.85 mmol) and 3.35 g of **4** (5.85 mmol) in 30 mL of a 2:1 acetonitrile−dichloromethane mixture was stirred at ambient temperature for 24 h. Evaporation of the solution in vacuo (0.02 mmHg at 295 K) generated a hard yellow oil. The yellow residue was triturated with hexanes, decanted, and dried in vacuo (0.02 mmHg at 295 K for 48 h) to yield 4.08 g (93.2%) of **5** as a fine yellow powder. ^1H NMR (chloroform-*d*, 300 MHz, δ): 2.42−2.75 (m, 4H, PCH_2); 3.29−4.06 (m, 16H, OCH_2); 7.71−7.00 (m, 20H, C_6H_5P). Anal. Calcd for $C_{34}H_{40}O_4P_2Cl_2Pd$: C, 54.31; H, 5.36; Cl, 9.40. Found: C, 54.41; H, 5.40; Cl, 9.52.

$^{31}P\{^1H\}$ NMR Spectroscopic Studies of the Dynamic Equilibria in Solutions of 5. Chloroform-*d* solutions of **5** with concentrations from 0.17 to 0.023 M were used in the equilibrium studies. A 0.17 M stock solution was prepared by dissolving 0.38 g (0.49 mmol) of **5** in 3.0 mL of chloroform-*d*. The NMR solutions were prepared by pipetting appropriate amounts of the stock solution into 5-mm, screw cap NMR tubes and by diluting to 0.6 mL with chloroform-*d*. The NMR tubes were then sealed with Teflon tape and stored in an oil bath whose temperature was regulated to ±1 K. The NMR tubes containing the solutions were placed in a pre-heated probe 30 min before acquisition of the $^{31}P\{^1H\}$ NMR spectra to ensure that spectra of equilibrium solutions were obtained. No solvent loss was observed in any sample during the course of the measurements.

Quantitative $^{31}P\{^1H\}$ spectra were acquired using an inverse-gated 30° pulse sequence with a 20-s delay and 3.8-s acquisition time. The inverse-gated pulse sequence, which eliminates NOE, was chosen because molecules with molecular weights in the range of 700−5400, like those in these experiments, may possess either positive, negative, or zero NOE.[18] The delay time necessary for quantitative spectra was determined directly by measuring the change in $^{31}P\{^1H\}$ integral area as a function of delay time in seconds. Empirically, a 20-s delay was found to be satisfactory for accurate measurement of species concentration via integration of the resonances. Accurate $^{31}P\{^1H\}$ NMR integral areas were calculated from the $^{31}P\{^1H\}$ NMR spectra using Bruker's UXNMR software. All quantitative $^{31}P\{^1H\}$ NMR spectra had a signal-to-noise ratio greater than 200:1 (calculated from the highest peak), which required acquisition times of 24 h for dilute samples.

A routine written with MATHCAD software was employed in the approximation of the equilibrium constants. All nonlinear approximations were calculated by minimizing the error function $\Sigma_{ss}([X_{Obs}] - [X_{Cal}])^2$ for each observable species and the overall formula concentration.

Results

Synthesis of Ligands and Complexes. The free ligands, $Ph_2P(CH_2CH_2O)_2CH_2CH_3$, **2**, and $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$, **4**, were prepared in good yields and high purities by the reactions of potassium diphenylphosphide with the corresponding methanesulfonates in dry tetrahydrofuran. These reactions are similar to those previously reported for the synthesis of **4**

(10) Varshney, A. Ph.D. Thesis, University of Alabama at Birmingham; 1992.
(11) (a) Minahan, D. M. A.; Hill, W. E. *Coord. Chem. Rev.* **1984**, *55*, 31−54. (b) Shaw, B. *J. Organomet. Chem.* **1980**, 200, 307−318.
(12) Hill, W.; Minahan, D. M. A.; McAuliffe, C. *Inorg. Chem.* **1983**, *22*, 3382−3387.
(13) Hill, W.; McAuliffe, C.; Niven, I.; Parish, R. *Inorg. Chim. Acta* **1980**, *38*, 273−278.
(14) Hill, W.; Taylor, J.; Falshaw, C.; Beagley, B.; Tonge, D.; Pritchard, R.; McAuliffe, C. *J. Chem. Soc., Dalton Trans.* **1986**, 2289−2295.
(15) (a) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856−3857. (b) March, F.; Mason, R.; Thomas, M.; Shaw, B. *J. C. S Chem. Commun.* **1975**, 584−585. (c) Pryde, A.; Shaw, B.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1976**, 322−327. (d) Pryde, A.; Shaw, B.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1973**, 947−948.
(16) Amman, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319−321.
(17) Varshney, A.; Webster, M.; Gray, G. M. *Inorg. Chem.* **1992**, *31*, 2580−2587.
(18) Harris, R. *Nuclear Magnetic Resonanace Spectroscopy*; John Wiley & Sons: New York, 1986, 85−90.

Table 1. $^{31}P\{^1H\}$ and Aliphatic $^{13}C\{^1H\}$ NMR Chemical Shifts for Ligands and Complexes

		C1		C2			
no.	P δ (^{31}P), ppm	δ (^{13}C), ppm	J(PC), Hz	δ (^{13}C), ppm	J(PC), Hz	C3,C4,C5 δ (^{13}C), ppm	C6 δ (^{13}C), ppm
2	−21.83 s	28.73 d	13[c]	68.57 d	25[d]	70.15 s, 69.76 s, 66.65 s	15.13 s
trans-**3**	12.32 s	25.84 aq	30[b]	66.55 aq	12[e]	69.95 s, 69.60 s, 66.49 s	15.04 s
cis-**3**	24.58 s	31.51 aq	35[b]	67.02 b	*f*	70.28 s, 69.56 s, 66.64 s	15.13 s
4	−21.73 s	28.73 aq	13[c]	68.53 d	25[d]	70.58 s, 70.53 s, 70.10 s	
M_t, **5**	13.56 s	26.69 aq	30[b]	67.02 aq	16[e]	71.36 s, 71.11 s, 70.25 s	

[a] b = broad, s = singlet, d = doublet, t = triplet, aq = apparent quintet, m = multiple overlapping singlets. [b] $|^1J(PC) + {}^3J(PC)|$. [c] $|^1J(PC)|$. [d] $|^2J(PC)|$. [e] $|^2J(PC) + {}^4J(PC)|$. [f] Ambiguous.

except that commercially available potassium diphenylphosphide was used in place of lithium diphenylphosphide (prepared in situ from diphenylphosphine and *n*-butyllithium solution). Both ligands are viscous oils that retain traces of solvent even under vacuum. The $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectral data of **2**, summarized in Table 1, have not been previously reported but are analogous to those of $Ph_2P(CH_2CH_2O)_2CH_3$.[19] The $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra of **4** have been reported,[1d] and selected spectral data are included in Table 1 for comparison purposes.

The complexes, $[PdCl_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_3\text{-}P\}_2]$, **3**, and $[PdCl_2\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]$, **5**, were prepared by reacting solid palladium(II) dichloride with the corresponding free ligand, **2** or **4**, in stirred acetonitrile−dichloromethane mixtures for 24 h at ambient temperature. Analytically pure **3** was obtained by recrystallization from dichloromethane−hexanes mixtures. Analytically pure **5** was obtained by trituration of the reaction residue with hexanes because attempts to recrystallize **5** were unsuccessful. These complexes are air-stable, orange-yellow solids that are slightly soluble in acetonitrile, methanol, and acetone and very soluble (>0.170 M) in tetrahydrofuran, dioxane, dichloromethane, and chloroform.

$^{31}P\{^1H\}$ NMR Spectra of the Complexes. The $^{31}P\{^1H\}$ NMR spectrum of **3** in chloroform-*d* contains two resonances at 12.32 and 24.53 ppm in a ratio of 6.6:1 at 308 K. The minor, downfield resonance is assigned to the cis isomer and the major, upfield resonance to the trans isomer. These assignments are consistent with those previously reported for other dichloropalladium(II) complexes with monodentate phosphine ligands.[19]

In contrast to the simple $^{31}P\{^1H\}$ spectra of **3**, the $^{31}P\{^1H\}$ NMR spectrum of **5**, shown in Figure 1, contains numerous resonances. These resonances are divided into three regions: several partially resolved resonances between 12.37 and 12.64 ppm, A; a single resonance at 13.56 ppm, B; and several overlapped resonances between 24.43 and 24.65 ppm, C. The integral areas of the resonances in regions A, B, and C are designated X_A, X_B, and X_C, respectively. All diphenylphosphino groups in **5** appear coordinated to palladium because no $^{31}P\{^1H\}$ NMR resonances due to free diphenylphosphino groups are observed.

The relative ratios of X_A, X_B, and X_C in the $^{31}P\{^1H\}$ NMR spectra of **5** exhibit a dynamic concentration and temperature dependence. As shown in Figure 2, the ratio of X_A to X_B decreases as the concentration of **5** is decreased from 0.17 to 0.023 M at constant temperature. In contrast, the ratio of ($X_A + X_B$) to X_C is independent of solute concentration at constant temperature. Both the ratio of X_B to X_A and the ratio of ($X_A + X_B$) to X_C increase as the temperature is increased.

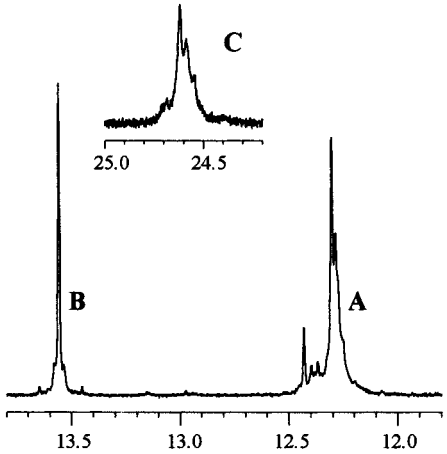

Figure 1. $^{31}P\{^1H\}$ NMR spectra of a 0.162 M solution of **5** (mol L^{-1}) at 295 K. Region A contains the resonances of the phosphines trans to phosphines in the *n*-mers. Region B contains the resonance of the trans monomer. Region C contains resonances for phosphines cis to phosphines in the *n*-mers and the cis monomer. Spectral parameters: chloroform-*d*, $^{31}P\{^1H\}$, 121.498 MHz; δ, ppm, S/N 268; NS, 128; LB, 0.0 Hz; SW, 1879.7 Hz; 30° pulse; delay, 1 s; aq time, 8.72 s.

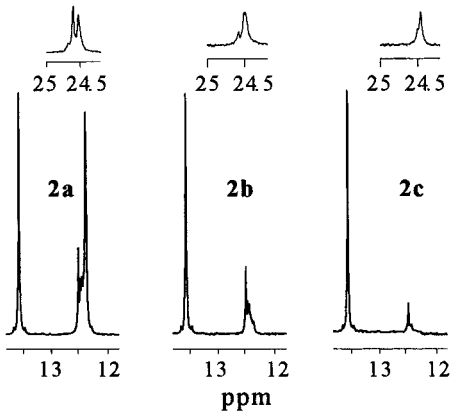

Figure 2. Quantitative $^{31}P\{^1H\}$ NMR spectra of equilibrated chloroform-*d* solutions of **5** at 0.143 M (**2a**), 0.072 M (**2b**), and 0.023 M (**2c**) total formula unit concentrations of **5** (mol L^{-1}). All measurements were taken at 308 K. Note the decreases in the intensities of the resonances in region A and the increase in the intensity of the resonance in region B as [**5**] decreases. Spectral parameters: chloroform-*d*, $^{31}P\{^1H\}$, 121.498 MHz; δ, ppm, (**2a**, S/N 648, NS 900; **2b**, S/N 325, NS 249; **2c**, S/N 265, NS 981); LB, 1.0 Hz; SW, 4273.5 Hz; 30° pulse; delay, 20 s; aq time, 3.83 s.

These observations suggest that solutions of **5** are equilibrium mixtures of cyclic *n*-mers and monomers with either cis or trans geometry, as depicted in Figure 3. The multiple resonances in region A are due to phosphines coordinated trans to other phosphines in the *n*-mers (these will subsequently be referred to as trans *n*-mers). The single resonance in region B is due to the trans monomer. The multiple resonances in region C are

(19) Reddy, V. V. S.; Whitten, J. E.; Redmill, K. A.; Varshney, A.; Gray, G. M. *J. Organomet. Chem.* **1989**, *372*, 207−215.

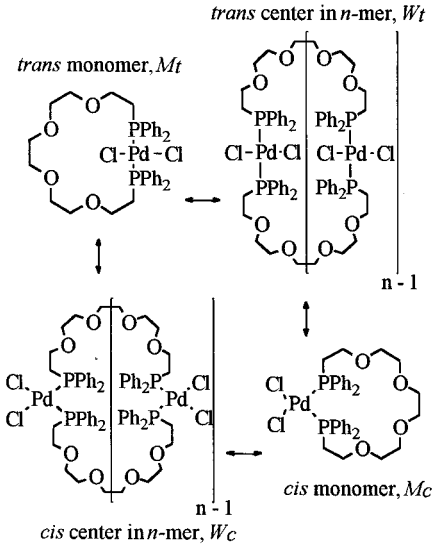

Figure 3. Proposed polymerization-isomerization equilibria in solutions of **5**.

due to phosphines coordinated cis to other phosphines in both the *n*-mers and the cis monomer (these will be collectively referred to as cis). At low solute concentrations, monomers are favored relative to *n*-mers, but the equilibria shift toward the *n*-mers as the concentration increases. As the temperature is increased, the *n*-mer/monomer equilibria shift toward the monomers, while the isomerization equilibria shift toward the trans isomers. This equilibrium behavior is consistent with the thermodynamics of cis−trans isomerization[20] and reversible polymerization.[21,22]

^{13}C{^{1}H} NMR Spectra of the Complexes. The ^{13}C{^{1}H} resonances of the C1 and C2 methylene carbons and the ipso, ortho, and meta phenyl aromatic carbons of the trans isomer of **3** are the A portions of AXX′ spin systems, while the analogous carbon resonances for the cis isomer are the A portions of AX spin systems.[23] This difference is apparently due to the absence of two-bond P−P coupling in the cis isomer. All other ^{13}C-{^{1}H} resonances for both isomers of **3** are singlets. Assignments for all ^{31}P-coupled ^{13}C{^{1}H} resonances in **3** are based on relative intensities and on comparison to the chemical shifts and coupling constants of related α,ω-bis(phosphine) complexes. The resonances of the C3 and C4 methylene carbons of **3** cannot be unambiguously assigned using this methodology.

The ^{13}C NMR spectra of solutions of **5** are more complex due to the multiple species present in the solutions. Assignment of the ^{13}C{^{1}H} NMR spectrum of the trans monomer, M_t, is possible because it is the major species present at low concentrations. In solutions of **5** at which significant concentrations of both monomers and *n*-mers are present, multiple resonances are observed for each of the carbons. As an illustrative example, the various ^{13}C{^{1}H} NMR resonances of the methylene carbons adjacent to the phosphines (C1) in **5** are shown in Figure 4. The ^{13}C{^{1}H} NMR resonances of the C1 methylene carbons in **3** are included in Figure 4 for comparison purposes.

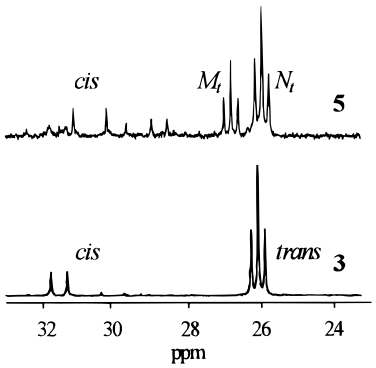

Figure 4. ^{13}C{^{1}H} NMR spectra for **3** and **5** at total formula unit concentrations of 0.17 M at 294 K illustrating the numerous resonances of C1, which are A portions of AXX′ or AX spin systems. Note that at least four different complexes with cis phosphines appear to be present in solutions of **5**. Spectral parameters: chloroform-*d*, ^{13}C{^{1}H}, 75.468 MHz; δ, ppm, (**5**, NS 17 000, LB 0.5 Hz; **3**, NS 20 000, LB 1 Hz); SW, 23 809.5 Hz; inverse gated 30° pulse; delay, 1 s; aq time, 1.37 s.

Table 2. Equilibrium Constants for Models I, II, and III in Chloroform-*d*[a]

	K_{ct}	K_1	K_2	K_3
		308 K		
I	5.2 ± 0.3			8.2 ± 1.7
II	5.3 ± 0.1	2.4 ± 0.5		19.1 ± 1.9
III	5.2 ± 0.1	3.1 ± 0.1	11.8 ± 3.4	20.0 ± 3.2
		331 K		
I	7.6 ± 0.6			6.2 ± 3.2
II	7.6 ± 0.3	2.0 ± 0.3		15.2 ± 1.3
III	7.9 ± 0.8	2.3 ± 0.4	10.3 ± 2.2	16.0 ± 2.3

Polymerization−Isomerization Equilibria for 5. To better understand the complex equilibria that exist in solutions of **5**, it is necessary to develop a model that explains the effects of concentration on the NMR spectra of the solutions. We have chosen the ^{31}P{^{1}H} NMR spectra for use in developing the model because quantitative ^{31}P{^{1}H} NMR spectra can be obtained in reasonable times and all the resonances in the spectra of **5** can be definitely assigned. Quantitative ^{31}P{^{1}H} NMR spectra were taken on six samples whose concentrations ranged from 0.17 to 0.023 M. One set of data was taken at 308 K and consisted of 19 measurements, while the second set was taken at 331 K and consisted of 17 measurements. For the two sets of concentration data, the sums of squares of residuals (SSR) and standard deviations (SD) have been calculated from multiple measurements of the integral areas, X_A, X_B, and X_C for all solutions. These are given in Table 3 on the lines labeled 308 and 331 K. The SSR and SD data indicate that the integrations of the quantitative ^{31}P{^{1}H} NMR spectrum are highly reproducible for both isothermal data sets.

The useful data in the ^{31}P{^{1}H} NMR spectra of **5** are the integral areas, X_A, X_B, and X_C, of the resonances in regions A, B, and C. These integral areas can be converted into the concentration of the trans monomer, $[M_t]$, the concentration of trans monomer formula units in all the *trans n*-mers, $[W_t]$, and the concentration of cis monomer formula units in both the cis monomer and *n*-mers, [cis], using eqs 1, 2, and 3, respectively.

$$[M_t] = \frac{X_B}{X_A + X_B + X_C} \times [\mathbf{5}] \quad (1)$$

In these equations, [**5**] is the concentration of total monomer units of all species present in the NMR solution of **5**.

(20) (a) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185−215. (b) Redfield, D. A.; Nelson, J. H. *Inorg. Chem.* **1973**, *12*, 15−19. (c) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50−59. (d) Cooper, D. G.; Powell, J. *Can. J. Chem.* **1973**, *51*, 1634−1644. (e) Verstuyft, A.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 1501−1505.
(21) Tolbolsky, A.; Eisenberg, A. *J. Am. Chem. Soc.* **1960**, *82*, 289−293.
(22) Sawada, H. *Thermodynamics of Polymerization*; Marcel Dekker: New York, 1976, pp 153−205.
(23) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lettt.* **1974**, *10*, 727−733.

Table 3. Sums of Squares of Residuals (SSR) and Standard Deviations (SD) from the Least-Squares Approximation of the Quantitative $^{31}P\{^1H\}$ NMR Spectra of **5** at Various Concentrations in Chloroform-*d* with Models I, II, and III[a]

	SSR $[W_t]$[b]	SSR $[M_t]$[b]	SSR [cis][b]	SD$[W_t]$[b]	SD $[M_t]$[b]	SD [cis][b]
308 K	2.87×10^{-7}	3.30×10^{-7}	1.22×10^{-7}	1.62×10^{-4}	1.73×10^{-4}	1.06×10^{-4}
I	5.49×10^{-3}	3.63×10^{-4}	1.54×10^{-4}	2.23×10^{-2}	5.74×10^{-3}	3.75×10^{-3}
II	2.22×10^{-3}	2.30×10^{-5}	5.29×10^{-5}	1.42×10^{-2}	1.46×10^{-3}	2.19×10^{-3}
III	2.20×10^{-3}	*c*	3.90×10^{-5}	1.41×10^{-2}	*c*	1.88×10^{-3}
331 K	2.23×10^{-7}	6.30×10^{-7}	1.50×10^{-7}	1.67×10^{-4}	2.81×10^{-4}	1.37×10^{-4}
I	4.51×10^{-3}	2.87×10^{-4}	5.33×10^{-5}	2.37×10^{-2}	5.99×10^{-3}	2.58×10^{-3}
II	1.21×10^{-3}	2.21×10^{-5}	1.61×10^{-5}	1.23×10^{-2}	1.66×10^{-3}	1.42×10^{-3}
III	1.21×10^{-3}	*c*	8.64×10^{-5}	1.23×10^{-2}	*c*	3.32×10^{-3}

[a] SSR and SD data in rows 308 K and 331 K are calculated for multiple measurements made on solutions with the same concentrations of **5** and provide an estimate of the reproducibility of the $^{31}P\{^1H\}$ NMR concentration measurements. [b] mol L^{-1}. [c] SSR and SD for $[M_t]$ were not calculated for III due to the nontrivial solution of eq 9.

$$[W_t] = \frac{X_A}{X_A + X_B + X_C} \times [\mathbf{5}] \quad (2)$$

$$[\text{cis}] = \frac{X_C}{X_A + X_B + X_C} \times [\mathbf{5}] \quad (3)$$

The next step in developing the model is to relate these concentration data to the equilibria shown in Figure 3. Four equilibria for the geometrical isomerization and step polymerization reactions of **5** are shown in Figure 3; however, the system can be uniquely defined with only three of these reactions. This description is further simplified because the cis−trans isomer ratio does not vary with concentration. Hence, the equilibrium constants for the cis−trans equilibria in monomers and various *n*-mers can be assumed to be identical.

The cis−trans isomerization equilibrium constant[20] of any monomer or *n*-mer is readily determined from $[W_t]$, $[M_t]$, and [cis], as shown in eq 4. However, determination of the

$$K_{ct} = \frac{[M_t] + [W_t]}{[\text{cis}]} \quad (4)$$

equilibrium constant(s) for the step polymerization of the trans monomer to higher *n*-mers is more complicated. A general reaction for step polymerization, in which the monomer, M_1, reacts with the *n*-mer, M_n, to form the $(n+1)$-mer, M_{n+1}, can be written as shown in eq 5. From this general equation,

$$M_1 + M_n \Leftrightarrow M_{n+1} \quad (5)$$

Tolbolsky et al. have derived eq 6, which relates the concentra-

$$[W] = \sum_{n=2}^{\infty} nK_1K_3^{n-2}[M_1]^n \quad (6)$$

tion of total formula units of monomer within all *n*-mers, [W], and the monomer concentration, $[M_1]$, to two equilibrium constants, K_1 for the dimerization reaction and K_3 for all higher polymerization reactions.[21,22] Power series expansion of eq 6 converges to the closed form, eq 7. In eq 7, the total

$$[W_t] = \frac{K_1[M_t]^2(2 - K_3[M_t])}{(K_3[M_t] - 1)^2} \quad (7)$$

concentration of all trans *n*-mers, $[W_t]$, and concentration of the trans monomer, $[M_t]$, have been substituted for [W] and $[M_1]$. It is significant to note that eq 7 differs from Tolbolsky's Case IIIa, in his general treatment of equilibrium polymerization, because Tolbolsky derived an approximate expression assuming a high degree of polymerization while eq 7 is an exact solution.[22]

There is no reason to assume a priori that two equilibrium constants correctly model the step polymerization equilibrium. Step polymerization with a single equilibrium constant can be modeled by equating K_1 and K_3 in eq 6. The power series expansion of eq 6 with K_1 replaced by K_3 converges to eq 8. It

$$[W_t] = \frac{2K_3[M_t]^2 - K_3^2[M_t]^3}{(K_3[M_t] - 1)^2} \quad (8)$$

is also possible to derive an equation, eq 9, in which the total

$$[W_t] = 2K[M_t]^2 + 3K_1K_2[M_t]^3 + \sum_{n=4}^{\infty} nK_1K_2K_3^{n-3}[M_t]^n \quad (9)$$

concentration of formula units within all trans *n*-mers, $[W_t]$, and the trans monomer concentration, $[M_t]$, are related to equilibrium constants for the dimerization reaction, K_1, the trimerization reaction, K_2, and for all higher polymerization reactions, K_3. The power series expansion of eq 9 converges to eq 10, which is valid for all degrees of polymerization.

$$[W_t] = \frac{K_1[M_t]^2(2K_3^2[M_t]^2 - 2K_2[M_t]K_3 - 4K_3[M_t] + 3K_2[M_t] + 2)}{(K_3[M_t] - 1)^2} \quad (10)$$

Equilibrium constants for the polymerization−isomerization reactions were calculated using the isomerization expression, K_{ct}, eq 4, and each of the three models of step polymerization described above (eq 8, model I; eq 7, model II; and eq 10, model III) by minimizing the appropriate nonlinear least-squares error functions ($\Sigma_{ss}([X_{Obs}] - [X_{Cal}])^2$). The equilibrium constants and absolute errors (at the 99% confidence level) are given in Table 2. A plot of the experimental $[M_t]$ values and the $[M_t]$ calculated from each of the three equilibrium models versus [**5**] is given in Figure 5. The sums of squares of residuals (SSR) and standard deviations (SD) from models I, II, and III for the approximation of $[W_t]$, $[M_t]$, and [cis] are given in Table 3 (mol L^{-1}). The SSR and SD for the *trans* monomer concentration, $[M_t]$, were not calculated for model III due to the nontrivial solution of eq 10 for the SSR and SD of $[M_t]$.

It is obvious from Figure 5 and the SSR and SD data in Table 3 that model I, with only one equilibrium constant for step polymerization, poorly models the equilibria concentrations of the various complexes in solutions of **5**, especially at higher solute concentrations. In contrast, both model II, with two equilibrium constants for step polymerization, and model III, with three equilibrium constants for step polymerization, accurately model the equilibrium concentrations of the various

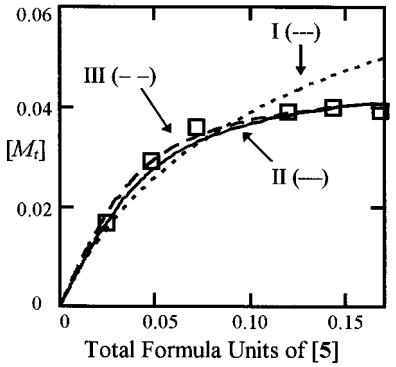

Figure 5. A plot of trans monomer concentration, $[M_t]$ (mol L^{-1}), versus the total formula unit concentration, [**5**] (mol L^{-1}) in chloroform-*d* at 308 K from models I, II, and III. The actual $[M_t]$ values are given by □. Note that models II and III are better approximations of $[M_t]$ than is model I at higher solute concentrations.

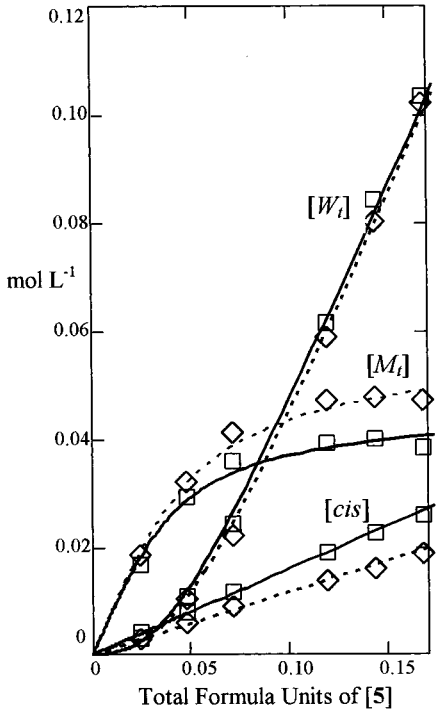

Figure 6. Trans monomer and *n*-mer and cis isomer equilibrium concentrations at 308 and 331 K as a function of overall solute concentration of **5** in chloroform-*d*. The equilibrium concentrations are calculated using model II. The experimental data are given by □ at 308 K and by ◇ at 331 K.

complexes over the entire concentration range. Because the addition of a third equilibrium constant for the step polymerization does not significantly improve the statistical description of the experimental data, model II appears to be sufficient to describe the equilibria in solutions of **5**. A plot of experimental and calculated (model II) $[M_t]$, $[W_t]$, and [cis] versus [**5**] at both 308 and 331 K is given in Figure 6.

One final point of interest is the distribution of *n*-mers in solutions of **5** at various concentrations. It is not possible to accurately determine this from the $^{31}P\{^1H\}$ NMR data because the resonances due to the various *n*-mers are overlapped. However, it is possible to predict this distribution using model II. This has been done for solutions of **5** at two concentrations (0.023 and 0.143 M, whose $^{31}P\{^1H\}$ NMR spectra are shown in Figure 2) and is shown in Figure 7. At the lower concentration, essentially the only *n*-mer present is the dimer, while at the higher concentration, a number of *n*-mers exist in solution.

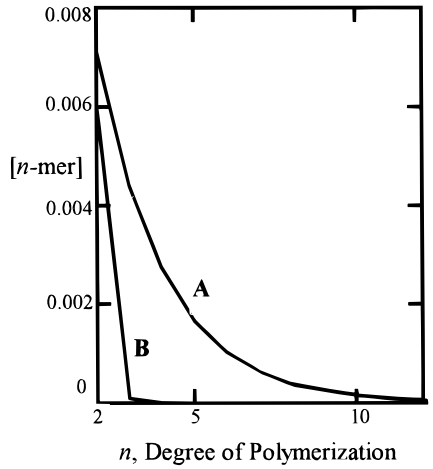

Figure 7. Estimation of the number-average concentration of trans *n*-mers, N_t (mol L^{-1}, calculated at total formula solute concentrations of **5** of 0.143 M, A, and 0.023 M, B, for chloroform-*d* solution at 308 K) using model II.

The approximations for *n*-mer concentration by model II are in qualitative agreement with the number of ^{31}P NMR resonances observed in region A for 0.023 and 0.143 M solutions of **5**.

***Cis*−*Trans* Equilibrium Constant for 5 in Acetonitrile-d_3.** The cis−trans equilibrium constant, K_{ct}, for **5** in acetonitrile-d_3 solution was calculated using eq 4. K_{ct} was determined to be 1.8 ± 0.3 at 308 K and 2.3 ± 0.3 at 331 K and was independent of the concentration of **5**.

***Cis*−*Trans* Equilibrium Constant for 3 in Chloroform-*d*.** The cis−trans equilibrium constant, K_{ct}, for **3** in chloroform-*d* was calculated from the integration of the $^{31}P\{^1H\}$ NMR resonances of the cis and trans isomers of **3** at two temperatures. The equation used to calculate K_{ct} for **3** was analogous to eq 4 but contained only the concentrations of the cis and trans monomers. The values calculated for K_{ct} of **3** were 6.6 ± 0.5 at 308 K and 9.5 ± 0.4 at 331 K. K_{ct} was found independent of the concentration of **3**.

Discussion

Thermodynamics of the Dynamic Equilibria in 5. The effect of temperature on the polymerization−isomerization equilibria in solutions of **5** is illustrated in Figure 6. As the temperature of the solution increases, the cis−trans isomerization equilibrium constant, K_{ct}, increases while both the dimerization equilibrium constant, K_1, and the *n*-merization constant, K_3, decrease. The increase in K_{ct} with increasing temperature is consistent with the behavior of cis−trans isomerization equilibrium constants of other bis(phosphine) dihalopalladium(II) complexes. The increase in K_{ct} is attributed to the fact that the maximization of solute−solution disorder favors the trans isomers in nonpolar solvents. The decreases in K_1 and K_3 with increasing temperature are as expected for reversible polymerization because entropy favors the monomer.[21,22]

The cis−trans isomerization equilibrium in **5** is also dependent on the polarity of the solvent (at 308 K, K_{ct} is 1.8 ± 0.3 in acetonitrile-d_3 and 5.3 ± 0.3 in chloroform-*d*). This is due to the fact that dipole−dipole interactions between the solvent and complex favor the cis isomers of **5** in polar solvents.[20]

The most interesting feature of the equilibrium constant data from model II is that the dimerization constant, K_1, is only 10% of the *n*-merization constant, K_3. This difference is unexpected and indicates that step polymerization is much more facile for *n*-mers of **5** than for the monomer of **5**. This is somewhat surprising because step polymerization for either the monomer

or an *n*-mer requires dissociation of the phosphine−palladium bond, and these bonds should have approximately the same strengths in the monomer and in the *n*-mers. One possible explanation for the difference in K_1 and K_3 is that the ether oxygens in the trans-spanning ligand of the monomer are oriented such that they can readily coordinate to the palladium once a diphenylphosphino group dissociates. The hemilabile coordination of the ether oxygen[24] would hold the diphenylphosphino group in the proximity of the palladium(II) center and favor coordination of the phosphine to the same palladium(II), to re-form the monomer, rather than coordination to a different palladium(II), to form an *n*-mer. In contrast, the ether oxygens in the *n*-mers should not be as close to the palladium(II) and would be less likely to coordinate when a diphenylphosphino group dissociates. Therefore, if the rates of phosphine dissociation of the monomer and *n*-mers are similar, the coordination of the ether oxygen would result in K_3 being larger than K_1 as is observed.

Other Palladium(II) Complexes with Long-Chain Bis(phosphine) Ligands. Our observation of dynamic cis−trans and monomer/*n*-mer equilibria for **5** is consistent with the results from other studies of palladium(II) complexes with long-chain bis(phosphine) ligands. Varshney has reported that the reactions of $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ ($n = 3, 5$) ligands with either bis(benzonitrile)dichloropalladium(II) or potassium tetrachloropalladate yielded numerous species, all with the empirical formula $[PdCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\}]$.[10] In contrast, Hill and co-workers have reported that the reaction of $Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2$ with lithium tetrachloropalladate yielded only the cis-monomeric complex.[14] Although cis−trans isomerization occurred upon halide metathesis, no polymerization was observed. This behavior may be due to the smaller macrocyclic ring in the $[PdCl_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2\}]$ complex.

Long-chain, bis(phosphine) ligands of the type $R_2P(CH_2)_nPR_2$ have been reported to form multiple complexes having the empirical formula $[PdCl_2\{R_2P(CH_2)_nPR_2\}]$. Shaw and co-workers were able to isolate monomeric ($x = 1$) and dimeric ($x = 2$) $[PdCl_2\{(^tBu)_2P(CH_2)_nP(^tBu)_2\}]_x$ ($n = 10, 12$) complexes from the reactions of the ligands with bis(benzonitrile)dichloropalladium(II) and potassium tetrachloropalladate.[15] Hill and co-workers have investigated the reactions of bis(benzonitrile)-dichloropalladium and potassium tetrachloropalladate with the $Ph_2P(CH_2)_nPPh_2$ ($n = 8, 10, 12$) ligands.[13,14] These reactions gave mixtures of products that were inseparable by chromatographic methods and, thus, were proposed to display dynamic behavior in solution.[14] Although both $[PdCl_2\{Ph_2P(CH_2)_8PPh_2\text{-}P,P'\}]$ and $[PdCl_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2\text{-}P,P'\}]$ possess eleven-membered macrocyclic rings, monomeric and *n*-meric complexes were observed with the $Ph_2P(CH_2)_8PPh_2$ ligand, whereas only the monomeric complex was observed with the $Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2$ ligand. The absence of *n*-mers in solutions of *cis*-$[PdCl_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2\}\text{-}P,P']$ suggests that the ether oxygen linkages in the ligand backbone favor formation of the monomer.

It is not possible to compare the degree of polymerization of **5** to those of the related complexes studied by Shaw and Hill. Both of these investigators used vapor-phase osmometry (VPO) to characterize the species present in solutions of the complexes and to estimate the degrees of polymerization of their complexes in solution.[12−15] If, as seems likely, dynamic equilibria are present in the solutions of these complexes, the degrees of polymerization reported by Shaw and Hill are not accurate because the relative amounts of monomers and *n*-mers will be different over the range of concentrations required for the VPO measurements.

Transition-Metal Complexes with Long-Chain α,ω-Bis(phosphine) Ligands. The nature of the complexes obtained from the reactions of long-chain α,ω-bis(phosphine) ligands with transition metal complex precursors is highly dependent upon the lability of the metal center and donor properties of the α,ω-bis(phosphine) ligand.[12] If, as is the case for the palladium(II) complexes, the reactions are under thermodynamic control, the same cis−trans and monomer/*n*-mer distributions will be observed regardless of the metal precursor complex and reaction conditions that are employed. In contrast, if the reactions are under kinetic control, the product distributions will be highly dependent on the donor properties of the ligand, chelate backbone length, reaction conditions, and metal precursor employed.[12] This appears to be the case for previously reported molybdenum(0), platinum(II), and ruthenium(II) metallacrown ethers and related platinum(II) complexes with long-chain bis(phosphine) ligands in which varied distributions of inert, separable monomer and *n*-mer complexes are obtained.[1,17,25]

Acknowledgment. Support of this work by the University of Alabama at Birmingham is gratefully acknowledged. D.C.S. thanks the Graduate School at UAB for a graduate fellowship. The authors wish to thank Mr. Fred Fish for helpful discussions concerning the derivation of the equilibria equations.

Supporting Information Available: Tables containing the $^{13}C\{^1H\}$ NMR aromatic chemical shifts for ligands and complexes (1 page). Order information is given on any current masthead page.

IC971249T

(24) (a) Linder E.; Schreiber, R.; Kemmler, H.; Mayer, A.; Fawzi, R.; Steinmann, M. *Z. Anorg. Chem.* **1993**, *619*, 202−211. (b) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27−110.

(25) (a) Hill, W.; Minahan, D.; Taylor, J.; McAuliffe, C. *J. Am. Chem. Soc.* **1982**, *104*, 6001−6005. (b) Salem−Al, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972−1982.